Design and Synthesis of Zero–Zero-Birefringence Polymers Using N-Methylmaleimide

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ABSTRACT: Zero–zero-birefringence polymers which exhibit no orientational birefringence and no photoelastic birefringence may be suitable candidates for the components of optical devices. To develop zero–zero-birefringence polymers, a novel copolymerization system is required. We investigated two types of birefringence of poly(N-methylmaleimide) (PMeMI) and showed that PMeMI exhibits positive orientational and photoelastic birefringence. On the basis of the results, we calculated the optimal composition for compensating both types of birefringence by solving three equations which describe the relationship between birefringence properties and weight fraction of monomers. When the copolymer compositions were MMA/BzMA/MeMI = 86/8/6 and 88/8/4 (wt %), zero–zero-birefringence polymers were obtained. By using MeMI as a comonomer, these zero–zero-birefringence polymers have a much higher glass transition temperature (T_g) than those of previous researches. Also, this polymer film has high transparency comparable with that of PMMA film. Therefore, we conclude that we successfully prepared zero–zero-birefringence polymers using N-substituted maleimide and that N-substituted maleimide is a promising material for zero–zero-birefringence polymers for optical devices. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40423.

INTRODUCTION

Polymer materials are widely used for various optical devices such as optical discs, lenses, and liquid crystal displays (LCDs) because of their light weight, low cost, and ease of processing compared with glass materials. However, polymer materials tend to exhibit birefringence, which means anisotropy of refractive index. Birefringence, which is induced during the manufacturing process and long-term use, degrades the performance of optical devices using polarized light, especially LCDs. Therefore, it is important to control the birefringence of polymer materials.

Birefringence of typical optical polymer materials is classified into two types, depending on the generation mechanism.[1] The first type of birefringence is orientational birefringence, which is caused by the orientation of the polymer main chain. Polymer chains have their own intrinsic anisotropy of polarizability which comes from the anisotropy of polarizability of the monomer unit. When polymer chains orient randomly, polarizability of the chains is macroscopically isotropic and orientational bire-

fringence does not occur because the optical anisotropies of monomer units cancel each other out. However, when polymer chains orient in one direction, which typically occurs when a heated polymer is stretched above the glass transition temperature (T_g), the optical anisotropies of monomer units do not cancel each other out and orientational birefringence Δn_{or} occurs. The orientational birefringence is expressed by

$$\Delta n_{or} = \Delta n^0 \times f \tag{1}$$

where Δn^0 and f are the intrinsic birefringence and the degree of orientation of the polymer main chain, respectively. The second type of birefringence is photoelastic birefringence, which is caused by elastic deformation. The photoelastic birefringence Δn_{ph} is expressed by

$$\Delta n_{ph} = C \times \sigma \tag{2}$$

where C and σ are the photoelastic coefficient and the stress, respectively. Therefore, to eliminate birefringence it is essential to control both the intrinsic birefringence and photoelastic coefficient.

Tagaya et al. demonstrated zero–zero-birefringence polymers which exhibit no orientational birefringence and no photoelastic birefringence.[2–5] In previous researches, monomers with positive and negative birefringence that form polymers with positive and negative birefringence, respectively, were copolymerized and birefringence of the resulting copolymer was cancelled out when the composition of the monomers was optimized. The zero–zero-birefringence polymer was prepared by using a ternary copolymerization system consisting of methyl methacrylate (MMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), and benzyl methacrylate (BzMA).[2,3] This copolymer is free of both types of birefringence at any orientation of the polymer main chain or elastic deformation. The birefringence of a ternary copolymer can be controlled by the following three equations

$$\Delta n^0 = \Delta n_1^0 \times \frac{w_1}{100} + \Delta n_2^0 \times \frac{w_2}{100} + \Delta n_3^0 \times \frac{w_3}{100} \quad (3)$$

$$C = C_1 \times \frac{w_1}{100} + C_2 \times \frac{w_2}{100} + C_3 \times \frac{w_3}{100} \quad (4)$$

$$w_1 + w_2 + w_3 = 100 \quad (5)$$

where Δn_i^0, C_i, and w_i are the intrinsic birefringence, the photoelastic coefficient, and the weight fraction, respectively, of the ith polymer ($i = 1, 2, 3$). We determined the optimal composition for compensating for both types of birefringence by solving the equations under the condition $\Delta n^0 = C = 0$.

Zero–zero-birefringence polymers have the advantage that they do not change the polarization state of incident light. On the other hand, a zero–zero-birefringence polymer which is designed in a ternary copolymerization system has the disadvantage that the composition of monomers is fixed and it is not possible to control other characteristics. Therefore, in some previous researches, various copolymerization systems consisting of three or four methacrylate monomers were proposed for designing zero–zero-birefringence polymers. However, a zero–zero-birefringence polymer in a copolymerization system containing monomers other than methacrylate monomers has not been demonstrated yet. Thus, a novel copolymerization system containing monomers other than methacrylate monomers is needed for the development of a zero–zero-birefringence polymer with the appropriate characteristics for optical devices.

N-substituted maleimides (RMIs) are known to have high heat resistance. Homopolymers of RMIs and their copolymer with methacrylate monomers or styrene have been reported to have a high glass transition temperature and thermal stability.[6–11] However, few previous researches have focused on the birefringence of RMIs.[12–14]

In this article, we propose N-methylmaleimide (MeMI) as a constituent of a ternary copolymerization system for designing a zero–zero-birefringence polymer. First, the intrinsic birefringence Δn^0 and the photoelastic coefficient C of PMeMI are investigated. Then, by using MeMI as a comonomer, a zero–zero-birefringence polymer is designed in a ternary system consisting of MMA, BzMA, and MeMI. We synthesize the copolymer and evaluate its birefringence and other characteristics.
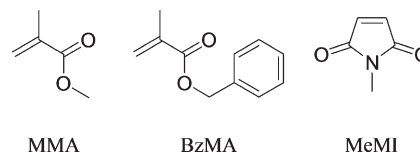

Figure 1. Chemical structure of monomers.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), benzyl methacrylate (BzMA), and N-methylmaleimide (MeMI) were purchased from Mitsubishi Gas Chemical (Tokyo), Wako Pure Chemical Industries (Osaka), and Tokyo Chemical Industry (Tokyo). The chemical structures of monomers are shown in Figure 1. The initiator 1-$tert$-butyl-3-(2-ethylhexanoyl)trioxidane (PBO) was purchased from NOF (Tokyo) and chain transfer agent butanethiol (BuSH) was purchased from Wako Pure Chemical Industries. The solvents methanol and dichloromethane were also purchased from Wako Pure Chemical Industries. The MMA monomer was freshly distilled before use; all other chemicals were used without further purification.

Preparation of Polymer Samples

To investigate the birefringence properties of PMeMI, we synthesized samples of poly(MMA-co-MeMI) with various composition ratios from 10 to 50 wt % of MeMI by means of bulk polymerization. All polymerization reactions were carried out at 70°C in a water bath for 24 h and then at 90°C in a drying machine for 24 h with 0.4 wt % of PBO as an initiator and 0.1 wt % of BuSH as a chain-transfer agent. The obtained polymers were purified by dissolution in dichloromethane and precipitation in a large volume of methanol. Then, the precipitated polymer was dried at room temperature for 24 h and then at 90°C under reduced pressure for 24 h. The purified polymers were made into films by dissolving poly(MMA-co-MeMI) in dichloromethane and spreading the polymer solution onto a glass plate with a knife coater. The films were dried at room temperature for 1 h and then at 90°C for 24 h under reduced pressure to remove the solvent. The resulting polymer films were cut into dumbbell-shaped specimens.

To determine the monomer reactivity ratios of MeMI with the other two monomers, we synthesized samples of poly(MMA-co-MeMI) and poly(BzMA-co-MeMI) with various composition ratios from 5 to 50 mol % of MeMI by means of bulk polymerization. All polymerization reactions were carried out at 70°C in a water bath for 1–3 h with 0.4 wt % of PBO as an initiator and 0.1 wt % of BuSH as a chain-transfer agent. The conversion of each copolymer was restricted to <10 wt % to ensure a homogeneous composition. The resulting polymers were precipitated by pouring the reaction mixtures into methanol and the precipitated polymer was then dried at room temperature for 24 h and then at 90°C under reduced pressure for 24 h. All polymers were purified by dissolution in dichloromethane and precipitation in a large volume of methanol. The compositions of poly(MMA-co-MeMI) and poly(BzMA-co-MeMI) were determined by means of ^{13}C NMR spectroscopy and ^1H NMR spectroscopy, respectively.

(a) Orientational birefringence

(b) Photoelastic birefringence
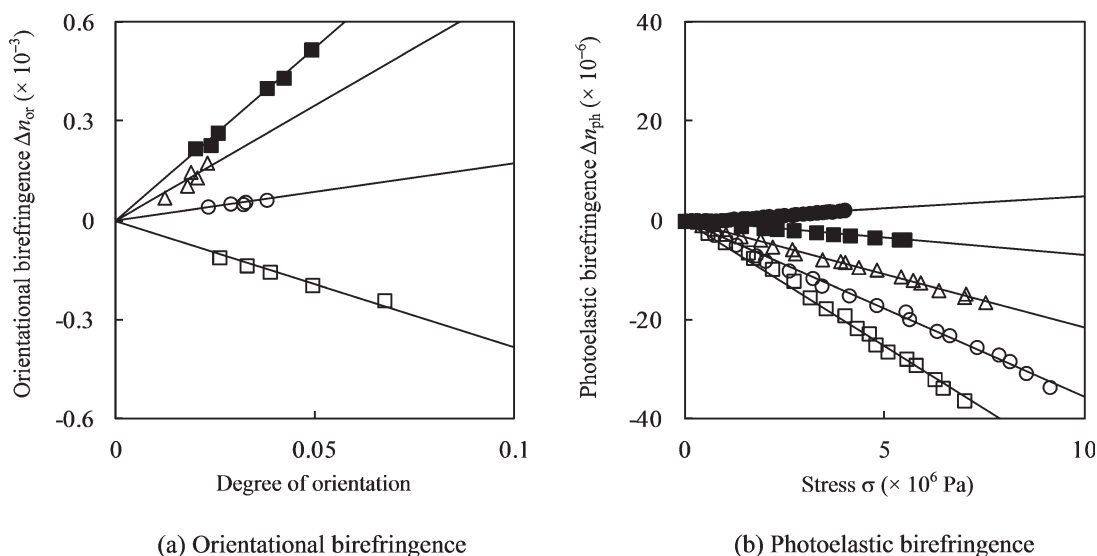
Figure 2. Birefringence of poly(MMA-co-MeMI). The proportion of MMA monomer in the feed was 60 (•), 70 (■), 80 (△), 90 (○), or 100 (□) wt %.

From the result of calculating the optimal composition ratios for eliminating both types of birefringence, ternary copolymers of MMA, BzMA, and MeMI with the optimal compositions were synthesized, purified, and fabricated into films in the same way as described above for the binary copolymers.

Measurement of Orientational Birefringence

To investigate the relationships between degree of orientation and orientational birefringence of the polymer samples, each fabricated film was uniaxially heat drawn above its T_g by using a universal tensile testing machine (Tensilon RTC-1210A; A&D, Tokyo). The orientational birefringence Δn_{or} of the uniaxially stretched films was measured at room temperature by optical

heterodyne interferometry at a wavelength of 633 nm by using a birefringence measurement device (ABR-10A; UNIOPT).[15] The sign of the orientational birefringence is defined as $\Delta n_{or} = n_{||} - n_{\perp}$, where $n_{||}$ and $n_{\perp}$ are the refractive indices of light polarized in the directions parallel and perpendicular to that of the heat drawing, respectively. The degree of orientation was determined by measuring the IR dichroism of the uniaxially stretched films at room temperature. The absorbance of the films was measured at 400–4000 cm^{-1} by using a polarizing Fourier-transform IR spectrometer (7000e FT-IR; Varian, Palo Alto, CA). The absorbance of the polarized IR radiation was measured in the directions parallel and perpendicular to the drawing direction, which was assumed to correspond to the direction of the main chain

(a) Intrinsic birefringence

(b) Photoelastic coefficient
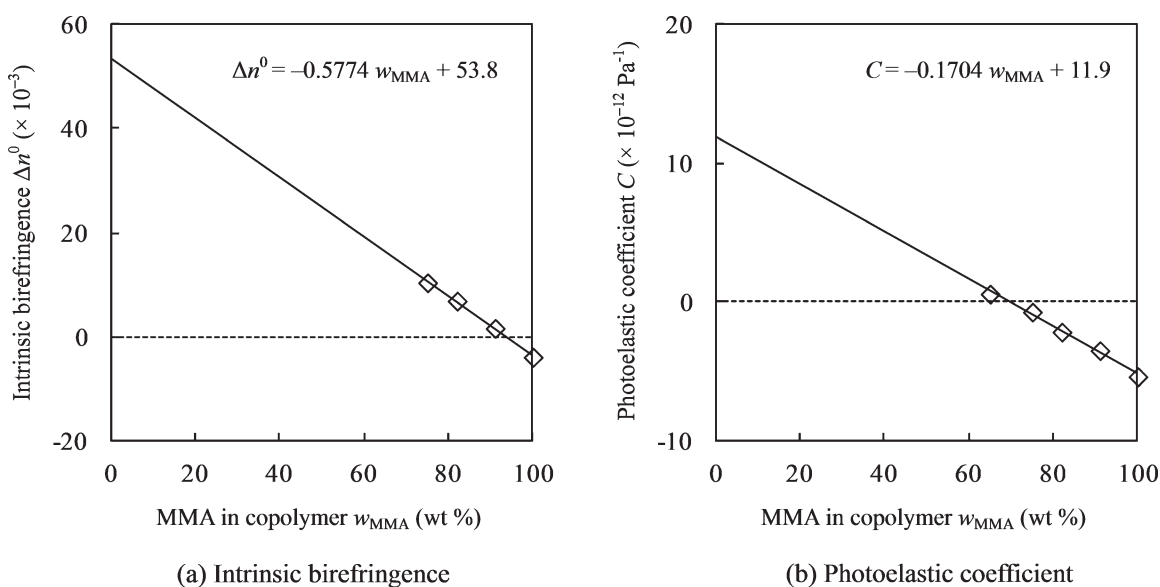
Figure 3. Birefringence properties of poly(MMA-co-MeMI). w_{MMA} is the proportion of MMA in the copolymer (wt %).
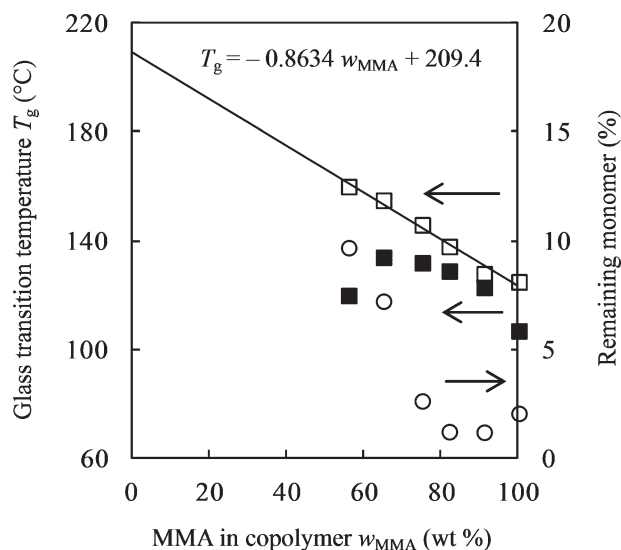
Figure 4. Glass transition temperature of bulk (■) and purified (□) poly(MMA/MeMI) and the amount of remaining monomer in bulk polymers (○). w_{MMA} is the proportion of MMA in the copolymer (wt %).
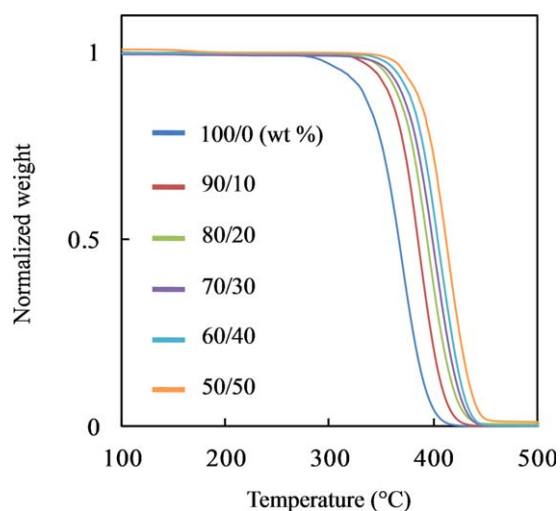
of the polymer. For this analysis, we selected a wavenumber of 750 cm^{-1}, which corresponds to the rocking vibration of the CH$_2$ group.[16] The dichroic ratio D is defined as

$$D = \frac{A_{//}}{A_{\perp}} \quad (6)$$

where $A_{||}$ and $A_{\perp}$ are the absorbances of the polarized IR radiation in the directions parallel and perpendicular to the direction of drawing, respectively. The degree of orientation f is defined as

$$f = \frac{D-1}{D+2} \times \frac{2\cot^2\alpha + 2}{2\cot^2\alpha - 1} \quad (7)$$

where α is the angle between the transition moment vector of the absorbing group and the chain axis.[17] In the case of the rocking vibration of the CH$_2$ group at a wavenumber of 750 cm^{-1}, the angle is assumed to be 17°.[16] From the measured ori-

Table I. T_g, the Temperature of 5 wt % Loss, and 10 wt % Loss of Samples

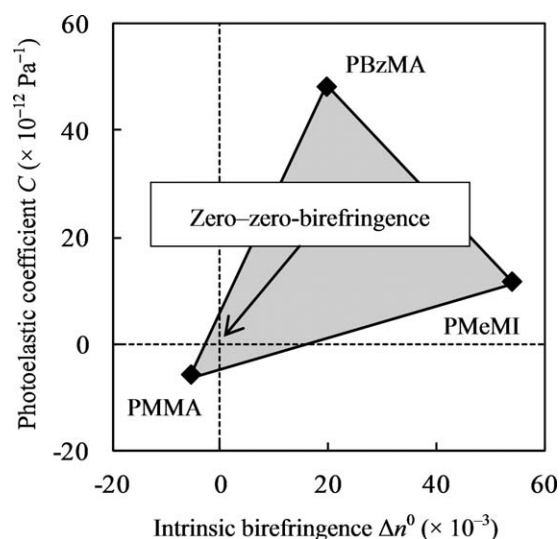| Polymer	T_g (°C)	5 wt % loss (°C)	10 wt % loss (°C)
PMMA	125	312	330
Poly(MMA/MeMI = 90/10 (wt %))	128	344	356
Poly(MMA/MeMI = 80/20 (wt %))	138	352	363
Poly(MMA/MeMI = 70/30 (wt %))	146	358	369
Poly(MMA/MeMI = 60/40 (wt %))	155	365	376
Poly(MMA/MeMI = 50/50 (wt %))	160	371	382

entational birefringence Δn_{or} and degree of orientation f, we determined the intrinsic birefringence Δn^0 by using eq. (1).

Measurement of Photoelastic Birefringence

The photoelastic birefringence Δn_{ph} of film samples in the upstretched state was measured at various levels of uniaxial tensile stress (about 1% strain) at room temperature by optical heterodyne interferometry at a wavelength of 633 nm by using a birefringence measurement system (ABR-10A; UNIOPT).[18] The stress was measured at the same time. The photoelastic coefficient C was determined from the relationship between the stress σ and the photoelastic birefringence Δn_{ph} given by eq. (2).

Other Measurements

We analyzed the composition ratios of poly(MMA-co-MeMI) by means of ^{13}C NMR spectroscopy (JNM-LA400; Nihon Denshi) in CDCl$_3$ as a reference. We also analyzed the composition ratios of poly(BzMA-co-MeMI) by means of ^{1}H NMR spectroscopy (AVANCEIII 600; Bruker) in CD$_2$Cl$_2$ as a reference. The T_g of each polymer was measured by using a differential scanning calorimeter (DSC-60; Shimadzu). All polymer samples were heated in air from room temperature to 200°C, held at 200°C for 5 min, then cooled to 80°C and reheated to 200°C at a scanning rate of 10°C min^{-1}. T_g was measured during the second

Figure 5. Thermogravimetric analysis of poly(MMA/MeMI) in N$_2$ stream. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]


Figure 6. Relationship between intrinsic birefringence and photoelastic coefficient.

Table II. The Intrinsic Birefringence Δn^0 and the Photoelastic Birefringence C of the Polymers[a]

Polymer	Intrinsic birefringence Δn^0 ($\times 10^{-3}$)	Photoelastic birefringence C ($\times 10^{-12}$)
PMMA	–5.6	–5.5
PBzMA	19.5	48.4
PMeMI	53.8	11.9

[a] The intrinsic birefringence and photoelastic coefficient of PMMA and PBzMA were analyzed in a previous work.[2]

heating scan. The weight percent of the remaining monomer in polymer bulks was measured by gas chromatography (GC-2010, Shimadzu). The polymer bulks were dissolved in a small amount of dichloromethane and then added to a large amount of methanol to precipitate the polymer. Based on the results of the gas chromatographic analyses of the supernatant liquid, the concentration of monomers was determined. Thermogravimetric analysis was carried out in N_2 stream by using a thermogravimetry and differential thermal analysis instrument (TG/DTA-6200, SII Nano Technology) at a scanning rate of $10°C$ min^{-1}. Transmittance spectra of polymer films were measured with a spectrophotometer (U-2800A; Hitachi). This spectrophotometer has a wavelength range of 190–1100 nm covered by a spectral bandwidth of 1.5 nm. The film thickness was 50 ± 5.0 μm. The haze of polymer films was measured by using a haze meter (NDH 2000; Nippon Denshoku Industries). The film thickness was 50 ± 5.0 μm. The orientational birefringence dispersion of the uniaxially drawn films was analyzed at six wavelengths (450.1, 497.2, 548.9, 585.8,
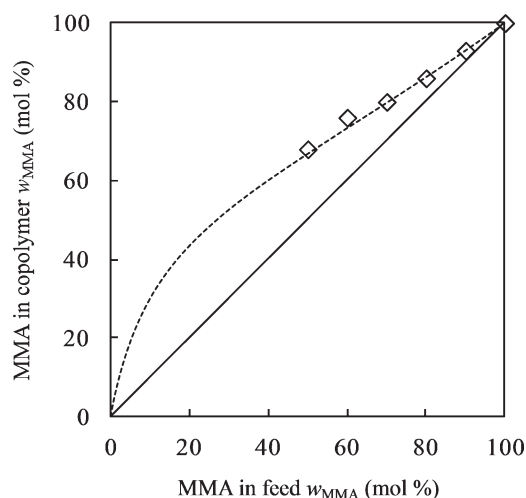

Figure 8. Relationship between the proportion of MMA in the feed (mol %) and the composition ratio of MMA in poly(MMA-*co*-MeMI). The solid and broken line represent the theoretical curves calculated by using $r_{12} = r_{21} = 1$ and $r_{12} = 1.39$, $r_{21} = 0.19$, respectively.

627.8, and 752.4 nm) by using a birefringence measurement device (KOBRA-WPR; Oji Scientific Instruments). The orientational birefringences at the selected wavelengths were fitted to the Sellmeier dispersion equation[19]:

$$\frac{\Delta n_{or}(\lambda)}{\Delta n_{or}(\lambda_0)} = \alpha + \frac{\beta}{\lambda^2 - \gamma^2} \qquad (8)$$

where $\Delta n_{or}(\lambda)$ and λ are the orientational birefringence and the wavelength, respectively; λ_0 is the wavelength for normalization (548.9 nm); and α, β, and γ are constants.
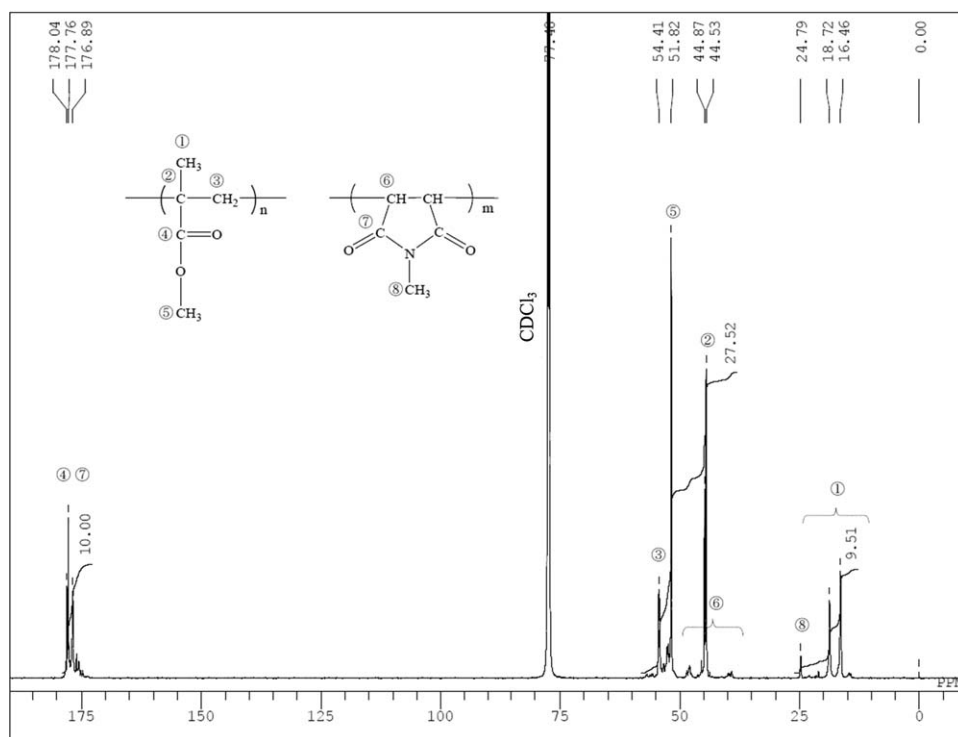
Figure 7. ^{13}C NMR spectra of poly(MMA/MeMI) with 90/10 (mol %) of the monomers in the feed.

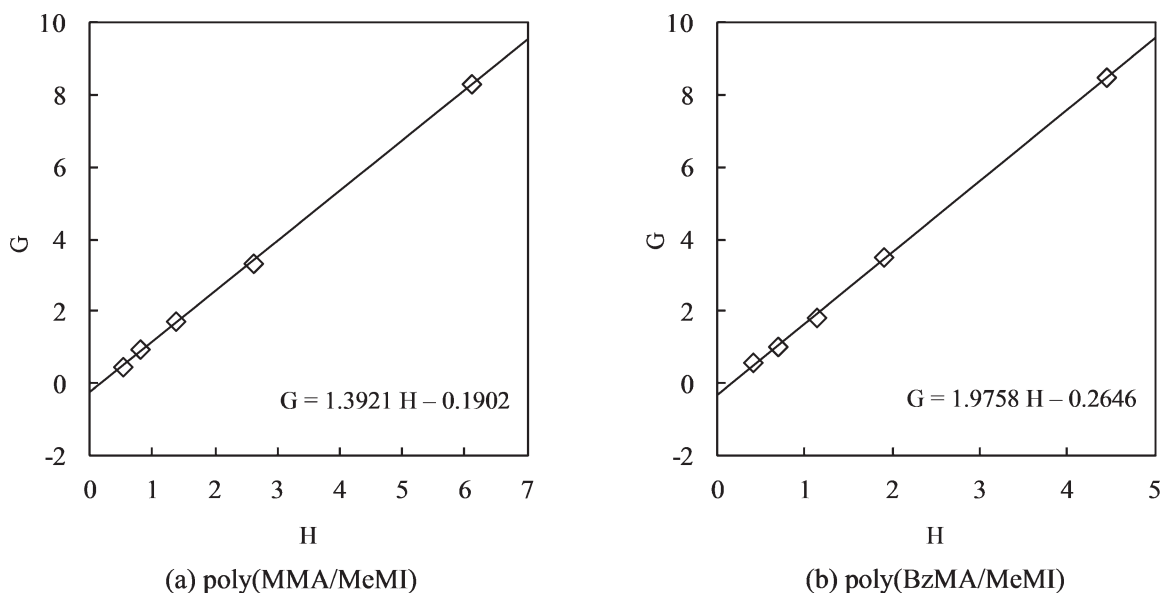(a) poly(MMA/MeMI)   (b) poly(BzMA/MeMI)

Figure 9. Fineman–Ross plot for poly(MMA-*co*-MeMI) and poly(BzMA-*co*-MeMI).

RESULTS AND DISCUSSION

Birefringence Properties of PMeMI

To design a zero–zero-birefringence polymer, the intrinsic birefringence and the photoelastic coefficient of PMeMI were determined. However, it was difficult to measure the birefringence properties of PMeMI directly because PMeMI is mechanically brittle. Therefore, we determined the birefringence properties of PMeMI by linear extrapolation of the change of birefringence properties of poly(MMA-*co*-MeMI) plotted against the proportion of MMA in the copolymer.

Figure 2(a) shows the orientational birefringence of poly(MMA-*co*-MeMI) samples with composition ratios of 100/0, 90/10, 80/20, and 70/30 by weight in the feed. The slope of each approximated line represents the intrinsic birefringence of each copolymer. Figure 3(a) shows the intrinsic birefringence plotted against the proportion of MMA, where w_{MMA} represents the proportion of MMA in the copolymers measured by ^{13}C NMR. The intercept of the approximated straight line (where the proportion of MMA is 0 wt %) represents the intrinsic birefringence of PMeMI. As shown in Figure 3(a), the intrinsic birefringence was estimated to be $\Delta n^0 = 53.8 \times 10^{-3}$.

Figure 2(b) shows the photoelastic birefringence of poly(MMA-*co*-MeMI) samples with composition ratios of 100/0, 90/10, 80/

20, 70/30, and 60/40 by weight in the feed. The slope of each approximated line represents the photoelastic coefficient of each copolymer. Figure 3(b) shows the photoelastic coefficient plotted against the proportion of MMA. By extrapolating the linear dependence, the photoelastic coefficient of PMeMI was estimated to be $C = 11.9 \times 10^{-12}$ Pa^{-1}.

As shown in Figure 3, the linear approximations agreed with the results of both birefringence properties. Therefore, the contribution of birefringence of each monomer unit is independent of the composition ratio of the copolymers.

Thermal Properties of PMeMI

Figure 4 shows the glass transition temperature (T_g) of bulk and purified poly(MMA-*co*-MeMI) samples with composition
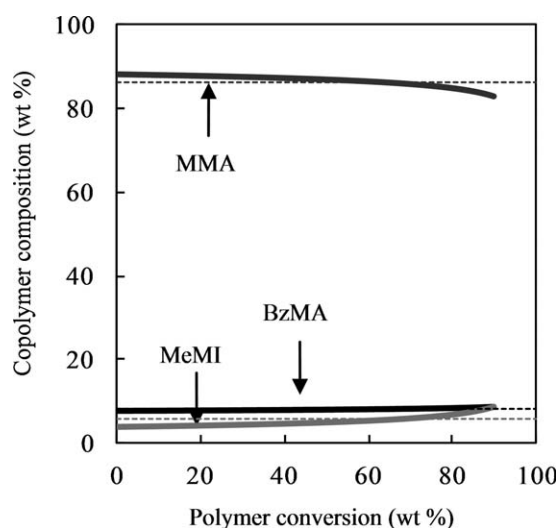
Table III. Fineman–Ross Parameters for Poly(MMA-*co*-MeMI)

$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$
9.00	13.29	8.32	6.10
2.60	6.14	3.35	4.00
2.33	4.00	1.75	1.37
1.50	2.85	0.97	0.79
1.00	1.94	0.48	0.52

M_1 and M_2 are the molar fractions of MMA and MeMI, respectively, in the feed, and m_1 and m_2 are the molar fractions of MMA and MeMI, respectively, in the copolymer.

Figure 10. Change in copolymer composition with polymerization conversion when the initial proportion of monomers in the feed was MMA/BzMA/MeMI = 86/8/6 (wt %). The broken line represents the initial composition ratio of each monomer.

Table IV. Monomer Reactivity Ratios of the Monomers[a]

	MMA	BzMA	MeMI
Monomer reactivity ratio	$r_{12} = 0.93$	$r_{21} = 1.05$	–
	$r_{13} = 1.39$	–	$r_{31} = 0.19$
	–	$r_{23} = 1.98$	$r_{32} = 0.26$

[a] The monomer reactivity ratios r_{12} and r_{21} were analyzed in a previous work.[2]

Table V. Haze Properties of the Ternary Copolymer Film and PMMA Film

Polymer	Haze (%)
Poly(MMA/BzMA/MeMI)	0.4
PMMA	0.2

The copolymer composition was MMA/BzMA/MeMI = 86/8/6 (wt %). The thicknesses of films were 50 ± 5.0 μm.

ratios of 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50 by weight in the feed. Figure 4 also shows the amount of remaining monomer plotted against the copolymer compositions of the samples. T_g of the bulk samples decreased when the bulks contained a lot of remaining monomer because of the plasticizing effect. On the other hand, T_g of the purified samples increased with the increasing proportion of MeMI because the remaining monomer was removed through the reprecipitation process. The intercept of the approximated straight line (where the proportion of MMA is 0 wt %) represents the T_g of PMeMI. As shown in Figure 4, T_g was estimated to be 209°C.

Figure 5 shows thermogravimetric curves of poly(MMA/MeMI). Poly(MMA) (PMMA) starts to decompose at lower temperature. On the other hand, the decomposition temperatures of the thermogravimetric curves are shifted to higher temperature as the composition of MeMI in the copolymer increases. The results of T_g measurement of purified polymers and thermogravimetric analysis are summarized in Table I.

Design of Zero–Zero-Birefringence Polymer
Figure 6 is a birefringence map showing the relationship between Δn^0 and C for the PMeMI and two methacrylate polymers. In a ternary copolymerization system, we can design a desirable birefringence inside a triangular area, and the origin of the map ($\Delta n^0 = C = 0$) represents zero–zero-birefringence. As shown in Figure 6, a novel zero–zero-birefringence polymer can be designed in the system because the three plots for PMMA,

poly(BzMA) (PBzMA), and PMeMI surround the origin of the map. The intrinsic birefringence and the photoelastic coefficient of each polymer are listed in Table II. By using these results, we calculated the composition of monomers to adjust both types of birefringence to zero, which was MMA/BzMA/MeMI = 86/8/6 (wt %).

Monomer Reactivity Ratios
To synthesize a zero–zero-birefringence polymer, the monomer constituents of the copolymerization system must copolymerize properly. The NMR spectrum of the poly(MMA-co-MeMI) is shown in Figure 7. The absorption corresponding to the resonance of the carbons of MMA (monomer 1) and MeMI (monomer 3) appears at 16.46–24.79 ppm, 44.53–54.41 ppm, and 176.89–178.04 ppm. We can determine the composition of the copolymers by comparing the intensities of these peaks. If we assume that the intensities at 16.46–24.79 ppm, 44.53–54.41 ppm, and 176.89–178.04 ppm are I_1, I_2, and I_3, respectively, the following equations can be applied to the copolymers:

$$I_1 = n + m \tag{9}$$
$$I_2 = 3n + 2m \tag{10}$$
$$I_3 = n + 2m \tag{11}$$
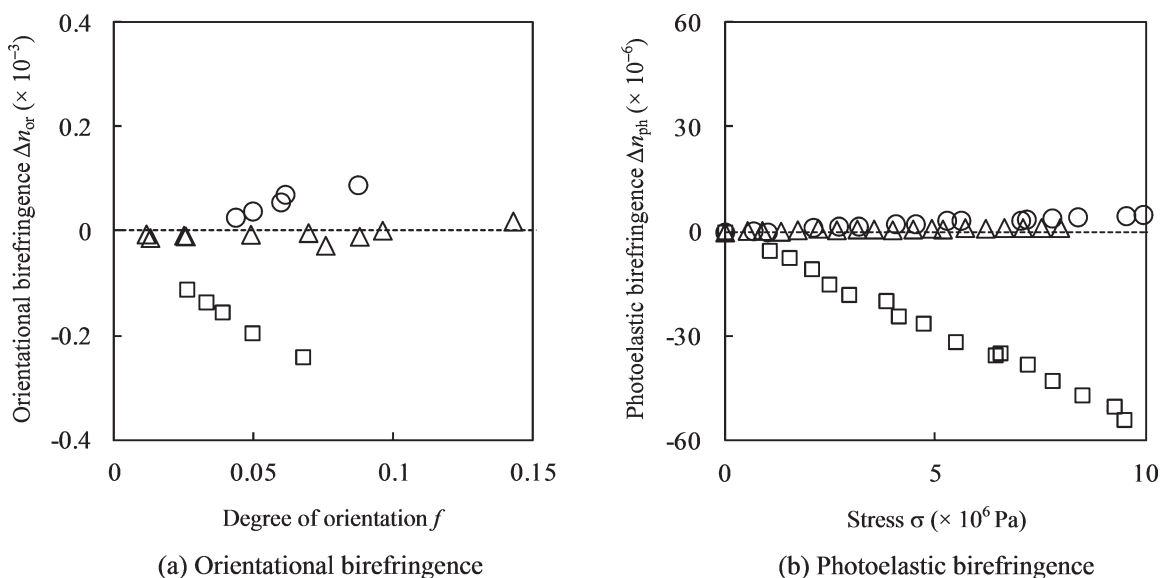
where n is the molar fraction of MMA in the copolymers and m is the molar fraction of MeMI in the copolymers. By measuring the intensities I_1, I_2, and I_3, the values of n and m can be calculated. Figure 8 shows the relationship between the composition of MMA in the feed (mol %) and that in the copolymers.

To determine the monomer reactivity ratios from the relationship between the monomer feed ratios and the copolymer composition ratios, we used the Fineman–Ross method.[20] The reactivity ratios of the monomers were determined by plotting the Fineman–Ross parameters G and H. The results are shown in Table III and Figure 9(a). The values of r_{13} and r_{31} (monomer 1: MMA; monomer 3: MeMI) obtained from Figure 9(a) are 1.39 and 0.19, respectively.

In the same way, the monomer reactivity ratios r_{23} and r_{32} (monomer 2: BzMA; monomer 3: MeMI) were determined from the results of analyzing the NMR spectra. The Fineman–Ross plots of poly(BzMA-co-MeMI) are shown in Figure 9(b). The monomer reactivity ratios of MMA, BzMA, and MeMI are summarized in Table IV.

Transparency of the Designed Copolymer
By using the results of analyzing the monomer reactivity ratios, we calculated the change of copolymer compositions through copolymerization. Figure 10 shows the change in copolymer

Figure 11. Transmittance spectra of the ternary copolymer film and PMMA film. The copolymer composition was MMA/BzMA/MeMI = 86/8/6 (wt %). The thicknesses of films were 50 ± 5.0 μm.

Figure 12. Birefringence of poly(MMA/BzMA/MeMI) and PMMA (□). The copolymer compositions were 86/8/6 (○) and 88/8/4 (△) (wt %).

compositions with the polymerization conversion as calculated by using the Mayo–Lewis equation[21] and the monomer reactivity ratios are listed in Table IV. The initial monomer composition in the feed was MMA/BzMA/MeMI = 86/8/6 (wt %); this is calculated to eliminate both types of birefringence. The details of the theory and calculation method are described elsewhere.[22,23] As shown in Figure 10, there is little change in the copolymer composition up to the termination of the polymerization (90 wt % conversion), which shows that monomers do not form homopolymers or alternating copolymers and that all the reactivity ratios are expected to be enough for proper copolymerization. Therefore, the ternary copolymers of these three monomers are expected to retain a high transparency because their largely heterogeneous structure implies that heterogeneity in the refractive index will not be generated.[22]

On the basis of the results, we synthesized a ternary copolymer with MMA/BzMA/MeMI ratios of 86/8/6 (wt %) and evaluated its transparency. The yield of the copolymer was about 90 wt %. The transmittance spectra of the copolymer film and that of PMMA film are shown in Figure 11. As shown, the transmittance of the copolymer film is 93.7% at the wavelength of 550

nm, whereas that of PMMA film is 93.4% at the same wavelength. The haze of the polymer films are shown in Table V. The haze measurements were carried out according to the American Society for Testing and Materials (ASTM) D1003. As can be seen in Figure 11 and Table V, the copolymer has a high transmittance (equal to that of PMMA) in the visible light range. Therefore, we conclude that the copolymer has sufficiently high transparency for optical films for LCDs.

Birefringence Properties of the Designed Copolymer
The orientational and photoelastic birefringence of the ternary copolymer were measured, with the results as shown in Figure 12 and Table VI. The copolymer was free of both types of birefringence, showing that we had successfully fabricated a zero–zero-birefringence polymer. Figure 12 and Table VI also show

Table VI. Birefringence Properties of the Zero–Zero-Birefringence Polymers and PMMA

Polymer	Intrinsic birefringence Δn_0 ($\times 10^{-3}$)	Photoelastic birefringence C ($\times 10^{-12}$ Pa^{-1})
Poly(MMA/BzMA/MeMI = 86/8/6 (wt %))	0.98	0.49
Poly(MMA/BzMA/MeMI = 88/8/4 (wt %))	–0.01	0.18
PMMA	–5.6	–5.5
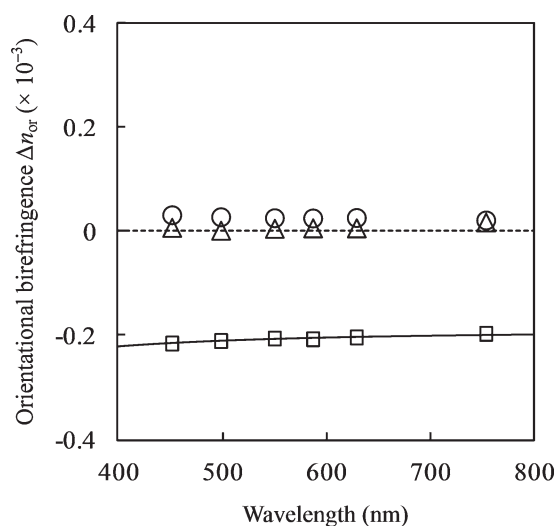
Figure 13. Wavelength dependence of the orientational birefringence of poly(MMA/BzMA/MeMI) and PMMA (□). The copolymer compositions were 86/8/6 (○) and 88/8/4 (△) (wt %).

Table VII. Thermal Properties of the Zero–Zero-Birefringence Polymers

Polymer	T_g (°C)	5 wt % loss (°C)	10 wt % loss (°C)
Poly(MMA/BzMA/MeMI = 86/8/6 (wt %))	120	344	353
Poly(MMA/BzMA/MeMI = 88/8/4 (wt %))	124	341	351

the results of measurements of the copolymer adjusted subtly from the calculated composition ratios for eliminating both types of birefringence.

Figure 13 shows the orientational birefringence dispersions of the zero–zero-birefringence polymers and that of PMMA. The degree of orientation of all the films was 0.05. For the PMMA film, the values of α, β, and γ in eq. (8) were obtained as follows: $\alpha = 0.924$, $\beta = 2.74 \times 10^4$, and $\gamma = 0$. The equation for the dispersion of the PMMA can be expressed as:

$$\frac{\Delta n_{\mathrm{or}}(\lambda)}{\Delta n_{\mathrm{or}}(\lambda_0)} = 0.924 + \frac{2.74 \times 10^4}{\lambda^2 - 0^2} \tag{12}$$

As shown in Figure 13, the PMMA film shows a normal dispersion, whereas the copolymers, regardless of the measurement wavelength, scarcely exhibited orientational birefringence.

Thermal Properties of the Designed Copolymer

Table VII shows the results of measurements of T_g, and the temperature of 5 wt % loss and of 10 wt % loss of the zero–zero-birefringence polymers. The copolymer with MMA/BzMA/MeMI ratios of 88/8/4 (wt %) exhibited higher T_g than the value reported in previous researches.[2–5]

CONCLUSION

For designing a zero–zero-birefringence polymer, MeMI was proposed as a constituent of a copolymerization system. Copolymer films of MMA and MeMI with various composition ratios were prepared and their two types of birefringence were analyzed. Based on the measurements, the intrinsic birefringence and the photoelastic coefficient of PMeMI were determined. We then calculated the optimal composition for compensating both types of birefringence in a copolymerization system consisting of MMA, BzMA, and MeMI. By means of the Fineman–Ross method, we confirmed the monomer reactivity ratios of these monomers. Based on the results, ternary copolymers with two different compositions of MMA/BzMA/MeMI (86/8/6, 88/8/4 (wt %)) were synthesized. These copolymers were shown to exhibit no orientational birefringence and no photoelastic birefringence. By using MeMI as a comonomer, these copolymers had much higher T_g than the zero–zero-birefringence polymers proposed in previous researches. Also, this copolymer film had high transparency comparable with that of PMMA film. Therefore, we conclude that zero–zero-birefringence polymers using N-substituted maleimide were successfully prepared and that N-

substituted maleimide is a promising candidate material for zero–zero-birefringence polymers for optical devices.

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